

## PATENT ABSTRACTS OF JAPAN

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## (54) LIQUID MODIFIED ETHYLENIC RANDOM COPOLYMER

## (57)Abstract:

PURPOSE: To obtain a liquid modified ethylenic random copolymer useful as a modifier or modification aid for various resins or rubber-like polymers, a lubricant additive or the like, by bonding an unsaturated carboxylic acid derivative component to an ethylenic random copolymer.

CONSTITUTION: This liquid modified ethylenic random copolymer is formed by bonding an unsaturated carboxylic acid derivative component (b) comprising a 3W10C unsaturated carboxylic acid or its anhydride or ester to an ethylenic random copolymer (a) composed of ethylene and a 3W20C  $\alpha$ -olefin. This copolymer satisfies the following requirements: (i) the ethylene component content of copolymer (a) is 10W85mol% and its  $\alpha$ -olefin component content is 15W90mol%, (ii) none and  $\alpha\beta$  and  $\beta\gamma$  signals ascribable to the methylene chain between two adjoining tertiary carbon atoms in the copolymer main chain is observed in a  $^{13}\text{C}$ -NMR spectrum of copolymer (a), and (iii) the content of component (b) is 0.2W50pts.wt. per 100pts.wt. copolymer (a).

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## English Translation of JP 07-078098 B2

## \* NOTICES \*

1. This document has been translated by computer using translation software, PAT-Transer V7 produced by Cross Language Inc. So the translation may not reflect the original precisely.
  2. The word which can not be translated is expressed by Japanese character.
  3. The drawings and tables are not translated.
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## [Claims for the Patent]

## [claim 1]

It is the liquid degeneration ethylene system random copolymer which unsaturation carboxylic acid derivative constituent comprising unsaturated carboxylic acid of number of carbon atom 3 - 10, the acid anhydride and the ester coupled in ethylene system random copolymer constructed as from ethylene and number of carbon atom 3 - 20  $\alpha$  - olefin and,

(i) Ethylene ingredient 10 of the ethylene system random copolymer - 85 mol % and  $\alpha$  - olefin ingredient 15 - a thing in a range of 90 mol %,

(ii) Signal of  $\alpha$   $\beta$  based on methylene linkage between two the third grade adjacent carbon atom in copolymer main chain and  $\beta$   $\gamma$  not being observed by the end of a  $^{13}\text{C}$ -NMR spectrum of the ethylene system random copolymer,

(iii) A component ratio of the unsaturation carboxylic acid derivative ingredient invites 0.2 - a thing in a range of 50 part by weight as against 100 part by weight of the ethylene system random copolymer

(iv) Limiting viscosity  $[\eta]$  0.01 measured in decalin of 135 degrees Celsius of the liquid property modification ethylene system random copolymer - a thing in a range of 0.4dl/g, the liquid degeneration ethylene system random copolymer which it is resembled, and, therefore, is characterized.

## [Detailed Description of the Invention]

## [Industrial Application Field]

The present invention is related to new liquid property modification ethylene system random copolymer. Even more particularly, liquid degeneration ethylene system random copolymer it be superior to color tone in detail and can show superior ability for use with dispersing agents of aqueous dispersion of modifying agent of various kinds of resin or a rubber-like polymer, reforming auxiliary, lubricating oil additive, resin or a rubber-like polymer is related to.

## [Prior Art]

The degeneration olefin system polymer that graft-copolymerization did unsaturated carboxylic acid or the acid anhydride in olefin system polymer of high molecular weight such as polyethylene, polypropylene conventionally is utilized for use with resinous modifying agent, adhesive property grant agent, others. However, because these property modification

olefin system polymer is high molecular weight body and is solid, when the ability which is enough by field of the invention is not provided, there is. In addition, the degeneration low molecular weight olefin system polymer that graft-copolymerization did unsaturation carboxylic acid derivative constituent such as unsaturated carboxylic acid, the acid anhydride, ester in olefin system polymer such as ポリブデン of low molecular weight, polyisobutylene is suggested to Japanese Patent Publication No. 52-23668 bulletin, Japanese Patent Publication No. 52-23669 bulletin, Japanese Patent Publication No. 52-48639 bulletin, but even if a rubber-like polymer utilizes the degeneration low molecular weight olefin system polymer for use with field such as dispersing agents of aqueous dispersion of modifying agent of a silicon component rubber-like polymer, reforming auxiliary, lubricating oil additive, resin or a rubber-like polymer particularly, superior ability is not shown. In a field of compounding technique of a rubber-like polymer in particular, that superior rubber-like polymer composition is provided is tried by blending ethylene /  $\alpha$  - olefin system or ethylene /  $\alpha$  - olefin system elasticity copolymer in rubber-like polymers such as natural rubber, polyisoprene, polyisobutylene, chloroprene be superior to antiweatherability, age resistance and and it is adhesive, but there is shortcoming that dynamics physical property of provided composition falls only by on that occasion having merely blended both both of, reforming auxiliary, in a typical example, to improve this shortcoming is blended. Even if, as this property modification auxiliary, olefin system polymer of the well-known property modification low molecular weight is blended conventionally, the effect is remarkable and is small.

[Problems to be solved by the Invention]

As a result that the people of present invention searched for modifying agent of various kinds of resin or a rubber-like polymer, degeneration low molecular weight ethylene system polymer particularly superior in rubber-like polymer composition as reforming auxiliary, liquid degeneration ethylene system random copolymer of a particular property is new high molecular material and that the rubber-like polymer composition and polio lev in, rubber-like polymer composition of dynamics physical property superior by what is blended as reforming auxiliary in resin such as polyethylene terephthalate or a reduced resin is provided is found, the present invention was arrived at. In addition, even if liquid property modification ethylene system random copolymer of the present invention is put in others for use with dispersing agents of aqueous dispersion of lubricating oil additive, resin or a rubber-like polymer, superior ability is shown.

[Means to solve the Problems] and [Operations]

The present invention is the liquid degeneration ethylene system random copolymer which unsaturation carboxylic acid derivative constituent comprising unsaturated carboxylic acid of number of carbon atom 3 - 10, the acid anhydride and the ester coupled in ethylene system random copolymer constructed as from ethylene and number of carbon atom 3 - 20  $\alpha$  - olefin and,

(i) Ethylene ingredient 10 of the ethylene system random copolymer - 85 mol % and  $\alpha$  - olefin ingredient 15 - a thing in a range of 90 mol %,

(ii) Signal of  $\alpha$   $\beta$  based on methylene linkage between two the third grade adjacent carbon atom in copolymer main chain and  $\beta$   $\gamma$  not being observed by the end of a  $^{13}\text{C}$ -NMR spectrum of the ethylene system random copolymer,

(iii) A component ratio of the unsaturation carboxylic acid derivative ingredient invites 0.2 - a thing in a range of 50 part by weight as against 100 part by weight of the ethylene system random copolymer

(iv) It is limiting viscosity  $[\eta]$  0.01 measured in decalin of 135 degrees Celsius of the liquid property modification ethylene system random copolymer - a thing in field of 0.4dl/g, the liquid degeneration ethylene system random copolymer which it is resembled, and, therefore, is characterized.

Liquid property modification ethylene system random copolymer of the present invention is the liquid degeneration ethylene system random copolymer which unsaturation carboxylic acid derivative constituent comprising unsaturated carboxylic acid of number of carbon atom 3 - 10, the acid anhydride and the ester coupled in ethylene system random copolymer constructed as from ethylene and number of carbon atom 3 - 20  $\alpha$  - olefin.

Preferably, as for the component ratio of an unsaturation carboxylic acid derivative ingredient of the liquid property modification ethylene system random copolymer, there is 0.2 - 50 part by weight in the range of 0.5 - 40 part by weight as against 100 ethylene system random copolymer part by weight. When component ratio 0.2 of an unsaturation carboxylic acid derivative ingredient blended as property modification auxiliary of rubber-like polymer composition if less than part by weight, improvement effect of physical property of dynamics of composition becomes inferior, flowability disappears if more than 50 part by weight again, color tone becomes bad and and it is solidified, dispersibility of a rubber-like polymer becomes bad again. Ester of unsaturated carboxylic acid such as acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid, tetrahydro phthalic acid, unsaturated carboxylic acid such as 2,2,1 5,6- bicyclo [ ] hept -2 - エン - dicarboxylic acid, maleic anhydride, itaconic acid anhydride, anhydrous Shirato Kon acid, tetrahydro phthalic anhydride, anhydride of unsaturated carboxylic acid such as 2,2,1 5,6- bicyclo [ ] hept -2 - エン - dicarboxylic acid anhydride, methyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, dimethyl maleate, maleic acid monomethyl, fumaric acid diethyl, dimethyl itaconate, citraconic acid diethyl, tetrahydro anhydrous dimethyl phthalate, 2,2,1 5,6- bicyclo [ ] hept -2 - エン - dimethyl can be exemplified for concreteness as number of carbon atom 3 which is an ingredient of the liquid property modification ethylene system random copolymer - ten unsaturation carboxylic acid derivative constituent unit.

Preferably there are as for limiting viscosity  $[\eta]$  0.01 measured in デリカン of 135 degrees Celsius of the liquid property modification ethylene system random copolymer - 0.4dl/g in the range of 0.02 - 0.3dl/g. Even if limiting viscosity  $[\eta]$  of the liquid property modification

ethylene system random copolymer shrinks than 0.01dl/g, and it grows bigger than 0.4dl/g, when it was blended as modifying agent of rubber-like polymer composition, improvement effect of physical property of dynamics of composition becomes inferior. In addition, lower than 4 are desirable for molecular weight distribution ( $M_w/M_n$ ) measured by gel soft-headed mi ray Chillon chromatograph E (GPC) of the liquid property modification ethylene system random copolymer, and it is field of less than or equal to 3. When if molecular weight distribution became too small, it was blended as property modification auxiliary of the rubber-like polymer composition, improvement effect of physical property of dynamics of composition shrinks.

Ethylene system random copolymer comprising the liquid property modification ethylene system random copolymer is liquid ethylene system random copolymer formed by  $\alpha$ -olefin of ethylene and number of carbon atom 3 - 20, and 10 - 85 mol %, is desirable for the ethylene constituent (a), and particularly preferably there is 20 - 80 mol %, in the range of 30 - 70 mol %, 15 - 90 mol %, is desirable for the  $\alpha$ -olefin constituent (b), and particularly preferably there is 20 - 80 mol %, in the range of 30 - 70 mol %. In addition, there is a non-conjugated polyene ingredient (c) other than an ethylene ingredient (a) and the  $\alpha$ -olefin ingredient if necessary when inter-polymerization is done liquid ethylene system random copolymer, 0 - 30 mol %, is usually desirable for content of non-conjugated polyene constituent (c) of that case, and particularly preferably there is 0 - 20 mol %, in the range of 0 - 15 mol %. When a total of constituent is 100 mol % with constituent (b) (a) when the ethylene system random copolymer is copolymer comprising an ethylene ingredient (a) and  $\alpha$ -olefin ingredients (b) here, and it is copolymer comprising ethylene constituent (a),  $\alpha$ -olefin constituent (b) and non-conjugated polyene constituent (c), a total of constituent and (c) constituent is 100 mol % constituent (b) (a).

0.01 0.4dl/g are usually preferable, and there is limiting viscosity  $[\eta]$  measured in デリカン of 135 degrees Celsius of the liquid ethylene system random copolymer in 0.03 - field of 0.3dl/g, in a typical example, preferably, as for the number average molecular weight, there are 300 - 8,000 in field of 500 - 5000, in a typical example, preferably, as for the molecular weight distribution ( $M_w/M_n$ ) which measured GPC method によつて, there are lower than 2.8 in field of less than or equal to 2.5 lower than 3 particularly. Even if content of an ethylene ingredient of ethylene system random copolymer of the liquid ethylene system random copolymer shrinks than 10 mol %, and content of a  $\alpha$ -olefin ingredient grows bigger than 90 mol %, even if content of ethylene constituent grows bigger than 85 mol % again, and content of  $\alpha$ -olefin constituent shrinks than 15 mol %, when the liquid degeneration ethylene system random copolymer was blended as reforming auxiliary of rubber-like polymer composition, improvement effect of physical property of dynamics of composition becomes inferior.

Propylene, one-butene, one-hexene, four-carbinyl-1-pentene, three-carbinyl-1-pentene, one-octene, one-decene, one-dodecen, one-tetradecene, one-hexadecene, one-octadecene, one-eicosen can be exemplified for concreteness as number of carbon atom 3 which is

component of the liquid ethylene system random copolymer - 20  $\alpha$  - olefin constituent. In addition, as a non-conjugated polyene ingredient, 1,4- hexadiene, 1,4- pentadiene, 1,7- octadiene, 1,8- nonadiene, 1,9- decadiene, four 1,4- carbonyl - hexadiene, five 1,4- carbonyl - hexadiene, five - ethylidene -2 - ノルボルネン, dicyclopentadiene, five - vinyl -2 - ノルボルネン, five - methylene -2 - ノルボルネン, 1,5- cyclo octadiene, 5,8- endo methylene hexahydronaphthalene can be exemplified to be concrete.

By the end of a  $^{13}\text{C}$ -NMR spectrum of the shaped ethylene system random copolymer, signal of  $\alpha$   $\beta$  based on methylene linkage between two the third grade adjacent carbon atom in copolymer main chain and  $\beta$   $\gamma$  is not observed.

By way of example only, follows are coupled to エチエン in copolymer with one - hexene:

Judging from the third grade carbon of left side coming from は, one - hexene, there is three central methylene group in  $\alpha$ ,  $\beta$ , location of  $\gamma$  from left side, judging from the third grade carbon of the on the other hand right side, there is in  $\alpha$ ,  $\beta$ , location of  $\gamma$  from the right side. That is why, by the end of the combination unit, there are  $\alpha$   $\gamma$  and methylene group giving a signal of  $\beta$   $\beta$ , but there is not methylene group giving signal of  $\alpha$   $\beta$  and  $\beta$   $\gamma$ .

The following bond which one - hexene comrade coupled by a tail vs. a head equally:

There is only the methylene group that being similar give  $\alpha$ , a signal of  $\alpha$ , there is not methylene group giving signal of  $\alpha$   $\beta$  and  $\beta$   $\gamma$ .

On the other hand, the following combination has the methylene group which gives signal of signal of  $\beta$   $\gamma$  and  $\alpha$   $\beta$  respectively.

A more liquid ethylene system random copolymer, equation described below (1)

During the ceremony of [, PE shows component mole fraction of an ethylene ingredient of copolymer, Po shows component mole fraction of  $\alpha$  - olefin constituent, PoE shows mole fraction of  $\alpha$  - オレフィン・エチレン linkage of all dyad linkage. But 0] which is the value that the component mole fraction of each ingredient in (I) type was calculated except an end ingredient)

B value which it attends, and is expressed,

A range satisfying 1.05 two equation described below  $(II) \leq B \leq \dots \dots (II)$  has.

It is indicator expressing distribution condition of each principal monomer distribution to be able to put by the end of copolymer chains, and B value is based on G.J.Ray (Macromolecules,10,773 (1977)), J.C.Randall (Macromolecules,15,353 (1982), J.Polymer Scinnce,Polymer Physics Ed.,11,275 (1933)), K.Kimura (Polymer,25,441 (1984)), a らの report, and it is calculated PE of the definition, Po and PoE by a request thing.

There are few block chains, and distribution of ethylene and  $\alpha$  - olefin is the same, and that it is small copolymer of composition part cloth is shown so that B value is big.

Preferably the liquid ethylene system random copolymer has B value as shown in follows.

Ethylene content of copolymer is a case of less than or equal to 50 mol %:

When preferably particularly preferably,  $1.0+0.3^* \text{ PE} \leq B \leq 1/ (\text{one} \cdot \text{PE})$ ,  $1.0+0.5^*$  general formula  $\text{PE} \leq B \leq 1/ (\text{one} \cdot \text{PE})$ , ethylene content of copolymer are more than 50

mol %  $1.0+0.4^*$  general formula  $PE \leq B \leq 1/(one - PE)$ :

Preferably particularly preferably,  $1.3-0.3^* 1/PE \leq B \leq PE$ , component cloth B value still measures spectra of  $^{13}C$ -NMR of the sample which made dissolve about 200mg copolymer in hexachlorobutadiene of 1ml in sample tubes of 10mm  $\phi$  uniformly under 4.2sec, seven pulse width  $\mu$  sec, the measurement condition of 2000-5000 times cost estimation frequency  $1.5-0.5^* 1/$  general formula  $PE \leq B \leq PE$   $1.4-0.4^* 1/$  general formula  $PE \leq B \leq PE$  for measurement temperature 120 degrees Celsius, measurement frequency 25.05MHz, spectra breadth 1,500Hz, filter breadth 1,500Hz, pulse time of repetition, it was calculated by here that demanded PE, Po, PoE from this spectra.

The liquid ethylene system random copolymer,

(A) The zirconium compound which assumed the basis having conjugate pi electron ligand, it is extended

(B) Because copolymerization succeeds in getting non-conjugated polyene as necessary, an existence bottom of a catalytic substance comprising alumino oxane can prepare.

In addition, number average molecular weight ( $\bar{M}_n$ ) of liquid ethylene system random copolymer of the present invention and molecular weight distribution ( $\bar{M}_w/\bar{M}_n$ ) follow written by Takeuchi, "gel permeation chromatograph E" of published by Matuzen, and it is line ivy like next.

(1) Using molecular weight known normal polystyrene  $\bar{M}_n$  monodisperse polystyrene made by Orient soda  $\bar{M}_n$ , molecular weight M and the GPC (Gel Permeation Chromatograph) count are measured, correlation diagram calibration curve of molecular weight M and EV (Elution Volume) is made. The density of this time assumes 0.02wt %.

(2) GPC chromatograph of sample is taken by the GPC measurement, and number average molecular weight  $\bar{M}_n$  of polystyrene conversion, weight average molecular weight  $\bar{M}_w$  are calculated by the (1), and  $\bar{M}_w/\bar{M}_n$  value is demanded. Sample preparation condition of the case and a GPC measurement condition are as follows.

[sample preparation]

(a) Fractionation does sample in Erlenmeyer flask with o-dichlorobenzene solvent to become 0.1wt %.

(b) 0.05wt % adds age resistor 2,6-di-tert-butyl-p-cresol in 入っている Erlenmeyer flask of sample as against polymer solution.

(c) Erlenmeyer flask is warmed to 140 degrees Celsius, it is stirred for about 30 minutes, it makes dissolve.

(d) The liquid is sprinkled in GPC.

[GPC measurement condition]

It was carried out under conditions of next.

(a) A product made in device Waters company (150 degrees Celsius - ALC/GPC)

(b) A product made in column Dupont company (ZORBAXPSM BiModal -)

(c) Sample quantity 200 $\mu$ l

(d) temperature 140 degrees Celsius

It was measured by GPC which number average molecular weight used molecular weight known standard substance (monodisperse polystyrene and squalane), and was made calibration beforehand which was (e) speed of flow 1ml/min.

Because heat reacts the liquid ethylene system random copolymer and the unsaturation carboxylic acid derivative (1) in an uncatalyzation bottom, an existence bottom of radical initiator can produce liquid property modification ethylene system random copolymer of the present invention by what is reacted again (2). Among these methods, it is preferable to adopt a method of (1). Liquid property modification ethylene system random copolymer provided by a method of (1) does the configuration which carboxylic acid derivative coupled in copolymer main chain end mainly.

It is drained off by a はなどを illustration again to be concrete.

An existence bottom of solvent can perform reaction, and a non-existence bottom of solvent can be performed.

While, for example, the unsaturation carboxylic acid derivative is mixed with liquid ethylene system random copolymer, and, for a reaction method, heat bottom continuation stirs, a method to react can be exemplified. Even more particularly, for the mixing method, a method liquid ethylene system random copolymer is divided, and consecutive, to add in a method, for example, the unsaturation carboxylic acid derivative is divided into liquid ethylene system random copolymer, and consecutive, to add, the adversely unsaturation carboxylic acid derivative can exemplify a method 10% does liquid ethylene system random copolymer and the unsaturation carboxylic acid derivative, and to be mixed. Preferably, as for the ratio of unsaturation carboxylic acid derivative supplied for the reaction, there is usually 0.2 - 100 part by weight in the range of 0.570 part by weight as against 100 part by weight of the liquid ethylene system random copolymer. 120 - 250 degrees Celsius are usually preferable, and there is temperature of case of reaction in the range of 130 degrees Celsius - 230 degrees Celsius, preferably time to need in reaction is usually for two hours - 30 hours for for one hour - 50 hours. Reaction can perform normal pressure, compression in both condition bottoms.

The use to field of application as modifying agent of rubber-like polymer composition of liquid property modification ethylene system random copolymer of the present invention is explained.

In the rubber-like polymer composition, it is constructed as from ethylene /  $\alpha$  - olefin system or ethylene /  $\alpha$  - オレフィン・ジエン system elasticity copolymer (A) or (A) and natural rubber, chloroprene rubber, isoprene rubber, butadiene rubber, at least one kind of rubber-like polymer (B) chosen by group comprising acrylic elastomer, the liquid degeneration ethylene system random copolymer (C) and other constituent (D). When the rubber-like polymer (B) is mixed with the elastic properties copolymer (A), preferably (A) there is usually (A) 5-95 part by weight and (B) 95-5 part by weight in the range of 10-90 part by weight and



(B) 90-10 part by weight, preferably, as for the combination rate of the liquid degeneration ethylene system random copolymer (C), there is 1 - 50 part by weight in the range of 5 - 30 part by weight for (A) and 100 part by weight of (B) in total.

Diene constituent content such as .5- ethylidene -2- ノルボルネン copolymer goddamn can usually exemplify 0.5 - ethylene /  $\alpha$  - olefin system elasticity copolymer in field of 4.5 mol % ethylene propylene copolymer, .1- ethylene butene copolymer, .4- ethylene carbonyl .1 - pentene copolymer, .1- ethylene hexene copolymer, crystallinity 0 such as .1- ethylene decene copolymer - ethylene /  $\alpha$  - olefin system elasticity copolymer of 10%, ethylene propylene dicyclopentadiene copolymer, .5- ethylene propylene ethylidene -2 - ノルボルネン copolymer, .1,4- ethylene propylene hexadiene copolymer, .1- ethylene butene dicyclopentadiene copolymer, ethylene .1- for elastic properties copolymer (A) blended by the rubber-like polymer composition.

Crosslinking agent, bridging accelerator, heat stabilizer resistance, stabilizer such as age resistor, filler can be given as other ingredients (D) blended by the rubber-like polymer composition to be concrete. A combination ratio of these ingredients is arbitrary.

Metal compound such as peroxide, sulfur, a - sulfur chloride, dichloride sulfur, モルホリンジスルフィド, アルキルフエノールジスルフィド, tetramethylthiuram disulfide, sulfur compound such as dimethyldithiocarbamic acid Se, magnesium oxide, zinc oxide, red lead can be given as crosslinking agent blended by the rubber-like polymer composition to be concrete. An ingredient usually as for the sulfur (A), preferably is used 0.1 - ten part by weight at the rate of 0.5 - five part by weight for 100 part by weight of a rubber ingredient comprising ingredients in total with an ingredient (B) (A). In addition, bridging accelerator can be used if necessary. For bridging accelerator, thiazole system such as N- cyclohexyl -2- ベンゾチアゾールスルフエンアミド, N- Oki ti diethylene -2- ベンゾチアゾールスルフエンアミド, N,N - diisopropyl -2- ベンゾチアゾールスルフエンアミド, two - mercaptobenzothiazole, two - (2,4- ニトロフェニル) mercaptobenzothiazole, two - (2,6- diethyl -4- モルホリノチオ) benzothiazole, ベンゾチアジルスルフィド, Guanidine system such as Ziv enyl guanidine, トリフェニルグアニジン, diortho tolyl guanidine, オルソトリルバイグアナイド, Ziv enyl guanidine phthalate, Acetaldehyde - aniline reactant, Butylaldehyde - aniline condensate, Hexamethylene tetramine, aldehyde amine such as acetaldehyde - ammonia or aldehyde - ammonia system, Imidazoline type such as two - mercapto imidazoline, チオユリア system such as チオカルバニリド, diethylthio lily horse mackerel butylthio urea, trimethylthio urea, diortho tolylthio urea, Thiuram system such as tetramethylthiuram monosulphide, tetramethylthiuram disulfide, テトラエチルウラムジスルフィド, テトラブチルチウラムジスルフィド, ジペンタメチレンチウラムテトラスルフィド, Dithioic acid salt system such as dimethyldithiocarbamic acid zinc, diethylthio carbamic acid zinc, di-n- butyl dithiocarbamate zinc, エチルフエニルジチオカルバミン acid zinc, ブチルフエニルジチオカルバミン acid zinc, dimethylthio carbamic acid sodium, dimethylthio carbamic acid Se, diethyldithiocarbamate Te, Xanthate system such as dizinc butylxanthate can be given.

An ingredient as for the these bridging accelerator (A), preferably is usually used 0.1 - 20 part by weight at the rate of 0.2 - ten part by weight for 100 part by weight of rubber constituent comprising ingredients in total with an ingredient (B) (A).

As peroxide used by peroxide bridging, dicumyl peroxide, 3,3,5-1,1'-di(t-butyl peroxy)-trityl cyclohexane, di(t-butyl peroxy) diisopropyl benzene, 2,5-dimethyl-2,5-di(t-butyl peroxy) hexane, 2,5-dimethyl-2,5-di(t-butyl peroxy) ヘキシンは exemplified.

In addition, independent, or, as bridging accelerator of the case, oxime chemical agent such as sulfur, sulfur compound such as ジペンタメチレンチウラムテトラスルフィド, ethylenedimethacrylate, divinylbenzene, diallylphthalate, メタフエニレンビスマレイミド, the poly pipe ability characteristics monomer which seem to be toluylene bismaleimide, p-chinone dioxime, p,p'-dibenzoyl chinone oxime is mixed, and it can be used.

Others can use activator, dispersing agent, filler, plasticizing material, adhesion bond agent, pigmenting drug, firing agent, firing auxiliary, lubricant, age resistor, others additive together in the rubber-like polymer composition if necessary.

For filler, inorganic filler such as carbon black, white carbon (Kay acid compound), calcium carbonate, purified talc, clay, Organic filler such as high styrene resin, coumarone and indene resin, Hue Nord resin, lignin, property modification melamine resin, petroleum resin can be given. Of these, it is preferable, and inorganic filler in particular is used.

Tenderizer pro-oil such as processing oil, lubricating oil, paraffin, flow paraffin, oil アスファルト, paraffin jelly for tenderizer, Coal tar system tenderizer such as coal tar, coal tar pitch, Fatty oil system tenderizer such as castor oil, linseed oil, a rapeseed oil, coconut oil, Tall oil, Sub, Dense low, Low such as カルナウバロウ, a refined wool fat, 12-hydroxyoleic acid, palmitin acid, barium stearate, calcium stearate, fatty acid such as zinc laurate and fatty acid salt, Synthetic polymeric substances such as petroleum resin can be given.

Sodium bicarbonate, ammonium carbonate, N,N'-dinitrosopentamethylenetetramine, azo carbonamido, azobisisobutyronitrile, benzene sulfonyl hydrazide, toluenesulfonyl hydrazide, calcium amide, para toluenesulphonylazide can use salicylic acid, phthalic acid, urea as plasticizing material for firing auxiliary for inorganic organic pigment to invite agent to fire at for colorant such as coumarone and indene resin, terpene Hue Nord resin, xylene formalin resin for agent it is adhered, and to bond to such as phthalic acid ester, adipic acid ester, sebacic acid ester, phosphoric acid system.

In addition, production of compound can adopt a well-known method to use open roll mill, Vamba Lee mixer, kneader.

Normal 100 degrees Celsius - 270 degrees Celsius are preferable, and preferably a bridging method can be performed under conditions of 1.5-60 minute in temperature of 120 degrees Celsius - 250 degrees Celsius for bridging length of time normal from 1 minute to 120 minutes. It is preferable to assume around 4 times of a half value period of peroxide in particular.

[Effects of the Invention]

Liquid property modification ethylene system random copolymer of the present invention shows superior ability as a dispersing agent of aqueous dispersion of modifying agent of resin or a rubber-like polymer, property modification auxiliary, lubricating oil additive, resin or a rubber-like polymer. Antiweatherability, heat aging resistance are adhesive, and be superior to ethylene /  $\alpha$  - オレフィン・ジエン system elastic properties copolymer (A) or (A) and rubber-like polymer composition comprising rubber-like polymers (B) by what is blended as reforming auxiliary in particular and physical property of dynamics has improved characteristic.

#### [Examples]

At first production of ethylene system random copolymer to use as raw materials in an example is explained by means of production example 1-5 concretely.

#### Production example 1

A thing (mole ratio 10 of Al/Zr, 0.04 mol / Zr / toluene) which continuous polymerization reactor of 2l is used, and processed 5mg atom /hr, bis (cyclopentadienyl) Zr thing hydride monochrome lide at trimethylaluminum in aluminium atom conversion in 0/hr, carbonyl alumino xanthan gum with refinement toluene 1 is supplied at the rate of  $8 \times 10^{-2}$  mg atom /hr in zirconium atom conversion serially, it is supplied at the rate of ethylene 40l/hr, propylene 240l/hr serially at the same time in polymerization vessel, it polymerized in polymerization temperature 40 degrees Celsius, permanent post detention time 1hr and the condition bottom where it was. Produced polymer solution is pulled out more continually than polymerization vessel, polymerization was stopped by adding a little methanol. Four times of operation a large quantity of water was added into the polymer solution, and to wash with water was repeated. Liquid ethylene-propylene rubber was got afterwards by removing toluene than polymer solution.

The liquid ethylene-propylene rubber provided with production example 1 used as copolymer of raw materials in example 1.

The polymer of production example 2-5 was provided by performing operation same as production example 1 under a condition of a list shown below.

Production example 2,3,4 mentioned in the top and the liquid copolymer provided with 5 used as copolymer of material in each example 3,4,5 and 6.

#### Production example 6

In production example 1, a polymer was got with ethylene, rate of feed of propylene respectively by assuming 240l/hr.

Cyclohexane 1 dilutes this polymer 100g, nickel catalytic substance 4g (N-103 made by day Teru chemistry) are added, a polymer was got by doing three 時間水添反応 at hydrogen pressure  $25 \text{ kg/cm}^2 \cdot \text{G}$ , 150 degrees Celsius.

This polymer used as copolymer of raw materials in comparative example 1.

Liquid property modification ethylene system random copolymer of the present invention is explained by means of an example concretely next.

### Example 1

After having substituted enough for product made in glass reactor with nitrogen inlet pipe, cooling pipe and agitator of internal space 500ml that loaded a thermometer with nitrogen, charge does ethylene content 43 mol %, propylene content 57 mol %, number average molecular weight 750,  $1.70 \text{ (Ow/O n)}$ ,  $[\eta]$  0.05dl/g, liquid ethylene propylene copolymer 200g and maleic anhydride 65g of 1.28 B value iodine value 33, it rose to 200 degrees Celsius in a stirring bottom. Reaction is cooled off to room temperature after line ivy at 200 degrees Celsius sequentially for eight hours, and reaction mixture is cast by the end of a large quantity of hexane, maleic anhydride of unreacting was removed. Furthermore, hexane is removed, liquid with the viscosity properties that was 淡黄透明 was provided by drying under subatmospheric pressure of 10mmHg at 100 degrees Celsius.  $[\eta]$  of the product extended to 0.05dl/g,  $\text{Ow/O n}$  1.95, and the content of a maleic anhydride ingredient was 1.1wt %. In addition,  $\alpha$   $\beta$ , the signal based on  $\beta$   $\gamma$  were not observed to a  $^{13}\text{C}$ -NMR spectrum of liquid ethylene propylene copolymer applied to reaction.

### Example 2

It was responded in much the same way as example 1 except that reaction temperature was assumed 180 degrees Celsius in example 1, and liquid with the viscosity properties that was pale yellow transparence was provided.  $[\eta]$  of the product extended to 0.05dl/g,  $\text{Ow/O n}$  1.83, and the content of a maleic anhydride ingredient was 6wt %. In addition, to a  $^{13}\text{C}$ -NMR spectrum of liquid ethylene propylene copolymer applied to reaction,  $\alpha$   $\beta$ , the signal based on  $\beta$   $\gamma$  were not observed.

Maleic anhydride constituent was not detected line ivy in much the same way as example 2 by product except that ethylene content 49 mol %, propylene content 51 mol %, number average molecular weight 830,  $1.44 \text{ (Ow/O n)}$ ,  $[\eta]$  0.05dl/g, B value 1.20, liquid ethylene propylene copolymer of iodine value 0 were used in one comparative example example 2. In addition,  $\alpha$   $\beta$ , signal based on  $\beta$   $\gamma$  were observed in  $^{13}\text{C}$ -NMR of liquid ethylene propylene copolymer applied to reaction.

Two drip Rohto is attached to reactor used in two comparative example example 1 more, liquid ethylene propylene copolymer 200g used with comparative example 1 were put, and it rose to 160 degrees Celsius. Time could write maleic anhydride 16g (it is kept warm to 60 degrees Celsius) that charge was made beforehand each and Jeter ti unpleasant Reeve till peroxide 3g 1.5 in two drip Rohto sequentially, and drip was done. After drip termination, reaction is raised to 180 degrees Celsius after line ivy at 160 degrees Celsius for four hours, the activity liquid which there was of content 6wt % of maleic anhydride constituent was provided 0.05dl/g,  $\text{Ow/O n}$  1.63  $[\eta]$  by removing decomposition product of maleic anhydride of unreacting and Jeter ti unpleasant Reeve till peroxide in an under vacuum of 0.5mmHg in the temperature. The product was colored transparent liquid in yellow.

### Example 3

It was performed in much the same way as example 2 except that 1,7- ethylene content 54

mol %, propylene content 42 mol %, octadiene content 4 mol %, number average molecular weight 820, 1.89 0w/0n,  $[\eta]$  0.05dl/g, B value 1.26, 1,7- liquid ethylene propylene - octadiene copolymer of iodine value 55 were used in example 2, and liquid with the viscosity which was pale yellow transparence was provided.  $[\eta]$  of the product extended to 0.05dl/g, 0w/0 n 2.05, and the content of a maleic anhydride ingredient was 10wt %. In addition,  $\alpha$   $\beta$ , the signal based on  $\beta$   $\gamma$  were not observed in  $^{13}\text{C}$ -NMR spectra of 1,7- liquid ethylene propylene - octadiene copolymer applied to reaction.

#### Example 4

It was performed in much the same way as example 1 except that ethylene content 62 mol %, hexene -1 content 38 mol %, number average molecular weight 970, 1.69 0w/0n,  $[\eta]$  0.06dl/g, liquid ethylene hexene -1 copolymer of 1.30 B value iodine value 26 were used in example 1, and liquid with the viscosity which was pale yellow transparence was provided.  $[\eta]$  of the product extended to 0.06dl/g, 0w/0 n 1.81, and the content of a maleic anhydride ingredient was 8wt %. In addition,  $\alpha$   $\beta$ , the signal based on  $\beta$   $\gamma$  were not observed in  $^{13}\text{C}$ -NMR spectra of liquid ethylene hexene -1 copolymer applied to reaction.

#### Example 5

Ethylene content 66 mol %, propylene content 34 mol %, number average molecular weight 3,570, 1.90 0w/0n,  $[\eta]$  0.24dl/g, B value 1.25, liquid ethylene propylene copolymer 200g and methacrylic acid n- butyl 25g of iodination 7 are taught reactor same as example 1, it is line ivy in reaction at 180 degrees Celsius for eight hours. Subsequently n- butylmethacrylate of unreacting is removed in an under vacuum of 10mmHg with having kept 180 degrees Celsius, liquid with viscosity was got in colorless extremely near transparently.  $[\eta]$  of the product extended to 0.25dl/g, 0w/0 n 2.07, and the content of a methacrylic acid n- butyl ingredient was 3wt %. In addition,  $\alpha$   $\beta$ , the signal based on  $\beta$   $\gamma$  were not observed to a  $^{13}\text{C}$ -NMR spectrum of liquid ethylene propylene copolymer applied to reaction.

#### Example 6

It is performed in much the same way as example 1 except that 1.80 ethylene content 55 mol %, propylene content 45 mol %, number average molecular weight 17000w/0n,  $[\eta]$  0.13dl/g, B value 1.28, liquid ethylene propylene copolymer of iodine value 15 were used in example 1, liquid with the viscosity which was pale yellow transparence was provided.  $[\eta]$  of the product extended to 0.14dl/g, 0w/0 n 1.96, and the content of a maleic anhydride ingredient was 5wt %. In addition, to a  $^{13}\text{C}$ -NMR spectrum of liquid ethylene propylene copolymer applied to reaction,  $\alpha$   $\beta$ , the signal based on  $\beta$   $\gamma$  were not observed.

#### Application 1

Product provided in example 1 was used as modifying agent when EPDM was blended with NBR. It is blended at the rate of 1+4 ENB system EPDM ( $\blacktriangle$  M100  $^{\circ}\text{C}$ , 67, 22 35 ethylene content 67 mol %, iodine value) part by weight, 65 NBR (ニツポール 1042) part by weight made in Nippon Zeon Corporation, ten product part by weight provided in example 1, zinc oxide 3-5 part by weight, one stearic acid part by weight, 60 product made in Asahi Carbon

Corporation carbon black (Asahi 70) part by weight, 15 dioctyl phthalate part by weight, 1.5 シクロヘキシルベンゾチアゾールスルフェンアミド part by weight, two 0.4 mercaptobenzothiazole part by weight, two diethylene glycol part by weight, 1.5 sulfur part by weight, and 8 inches open roll mill of skin temperature  $60 \pm 5$  degrees Celsius is used, it was kneaded in 20 minutes in lead time. JIS K6300 was followed, and Mooney viscosity of provided composition was measured.

Furthermore, the composition is heated at 160 degrees Celsius for 20 minutes, an abrasive sheet of  $150 \times 100 \times 2.5$  mm is made, JIS K6301 was followed, and spring hardness (Hs), tensile strength (Tb), strain under tension (Eb) were measured. A result was shown for table 1.

#### Application 2-5

Product provided with example 2 to 6 is used, and composition is synthesized with application 1 similarly, Mooney viscosity, Hs, Tb and Eb were measured. A result was shown for table 1.